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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

Date: December 10, 2003
Chemical: MCPA
PC Code: 030501
DP Barcode: D289864

Subject: **Data Evaluation Record (DER) for Aerobic Aquatic Metabolism in a Water/Sediment System Submitted in Support of MCPA**

To: Demson Fuller, Chemical Review Manager
Reregistration Branch I
Special Review and Reregistration Division (7508C)

From: Mark Corbin, Environmental Scientist
Environmental Risk Branch I
Environmental Fate and Effects Division (7507C)

12-10-03

Attached is the final Data Evaluation Record (DER) for the Aerobic Aquatic Metabolism study submitted in support of the re-registration of MCPA (PC Code 030501). The study has been deemed acceptable.

Data Evaluation Report on the aerobic biotransformation of MCPA in water-sediment system

PMRA Submission Number {.....} EPA MRID Number 45889303

Data Requirement: PMRA Data Code:
EPA DP Barcode: D289864
OECD Data Point:
EPA Guideline: 162-4

Test material:
Common name: MCPA.
Chemical name
IUPAC: (4-Chloro-2-methylphenoxy)acetic acid (Reviewer's Comment No. 7).
4-Chloro-o-tolyloxyacetic acid.
CAS name: (4-Chloro-2-methylphenoxy)acetic acid.
CAS No: 94-74-6.
Synonyms: Methyl-4-chlorophenoxy acetic acid.
CMP acetate.
Chloro-o-cresoxy acetic acid.
Metaxon.
SMILES string:

Primary Reviewer: Lynne Binari
Dynamac Corporation

Signature:
Date:

QC Reviewer: Kathleen Ferguson
Dynamac Corporation

Signature:
Date:

Secondary Reviewer: Mark Corbin
EPA

Signature:
Date: 12-9-03

Company Code: [for PMRA]
Active Code: [for PMRA]
Use Site Category: [for PMRA]
EPA PC Code: 030501

CITATION: Cremers, R.K.H. and F.G.Ch. Salmon-te Rietstap. 2003. Determination of the degradation of MCPA using [^{14}C]-MCPA in two water/sediment systems. Unpublished study performed by TNO Nutrition and Food Research, Delft, The Netherlands (p. 11); sponsored and submitted by MCPA Task Force III, Raleigh, NC. TNO Study No.: 4022/01 and Project No.: 010.46079/01.01. Experiment initiation May 2, 2002, and completion December 3, 2002 (p. 11). Final report issued March 7, 2003.

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EXECUTIVE SUMMARY:

The biotransformation of [phenyl-U-^{14}C]-labeled 4-chloro-2-methylphenoxy acetic acid (MCPA) was studied in ditch and river water-sediment systems (ditch and river water pH 8.3 and 8.0, respectively, water organic carbon not reported, sediments uncharacterized) from The Netherlands for 84 days under aerobic conditions in darkness at *ca.* 20°C. Based on the water volume, [^{14}C]MCPA was applied at a nominal rate of 0.8 mg a.i./L. The sediment:water ratios used were 1:4-4.5 (128-140 g dry wt. sediment:560-572 g water). This experiment was conducted in accordance with SETAC-Europe and Draft OECD 308 guidelines as specified by EU Commission Directive 95/36/EC and in compliance with OECD Principles of GLP, (ENV/MC/CHEM(98)17). The test system consisted of 1-L vessels containing water-sediment; all vessels, except day 0 systems, were fitted with an air-permeable trapping tower for the collection of CO_2 and volatile organic compounds. The water-sediment systems were pre-incubated for 19 days, then following treatment, duplicate samples were collected after 0, 1, 3, 7, 14, 28, 42 and 84 days of incubation. Water layers were filtered (cotton wool), then analyzed directly. Sediment samples were extracted one to four times with acetone:0.1M HCl, then extracts were combined and analyzed. Water layers, sediment extracts, extracted sediment, and trapping materials were analyzed for total radioactivity using LSC. Water layers and sediment extracts were analyzed for [^{14}C]MCPA and its transformation products by reverse-phase HPLC; [^{14}C]MCPA was identified by comparison to the retention time of unlabeled reference standard. Transformation products were not identified.

During the 84-day incubation, dissolved oxygen and pH in the water layers of both systems were 1.4-5.4 mg/L and 7.4-8.6, respectively; redox potentials of the water layers were not measured and sediment parameters were not determined.

Overall recoveries of radiolabeled material averaged (n = 16) 88.7 ± 13.0% (range 69.3-116.6%) and 100.1 ± 9.0% (range 82.0-117.6%), in the ditch and river water-sediment systems, respectively. Material balances steadily declined in the ditch water-sediment systems from 14 days posttreatment to study termination; however, there was no consistent decline in material balances in the river water-sediment systems. For both systems, [^{14}C]residues partitioned into the sediment with average (n = 2) distribution ratios (water:sediment) of ≥15:1 at 0-3 days, 6-7:1 at 7 days, 3:1 at 14 days, 1:5-7 at 28-42 days and were 1:≥9 at 84 days. For both systems, [^{14}C]MCPA in the total system was detected at 87.6-113.8% of the applied at 0-3 days, 82.5-101.1% at 7 days, 75.1-85.4% at 14 days, then decreased to 10.5-19.3% at 28 days, 7.3-11.8% at 42 days and was 3.6-5.8% at 84 days. In the water layers, [^{14}C]MCPA was detected at 87.0-110.9% of the applied at 0-3 days, 74.9-92.3% at 7 days, 55.8-67.9% at 14 days, 2.8-10.0% at 28 days, 3.9-5.4% at 42 days and 1.1-2.0% at 84 days. In the sediments, [^{14}C]MCPA increased from 0.3-1.5% at 0-1 days to 16.0-19.3% at 14 days, then decreased to 7.1-9.6% at 28 days, 2.7-7.3% at 42 days and was 2.1-3.8% at 84 days. Based on first-order linear regression analysis, MCPA (both systems) dissipated with reviewer-calculated half-lives of 12.3 days, 25.5-35.3 days and 16.3-16.8 days in the water layers, sediments and total systems, respectively,

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No major nonvolatile transformation products of MCPA were detected. Two minor unidentified [^{14}C]compounds of HPLC R_t = 4.5 and 6.7 minutes were detected in sediment extracts at 1.2-4.3% and 4.0-9.3% of the applied, respectively, at 28-42 days. Extractable [^{14}C]residues in both sediments increased from 0.3-1.5% of the applied at 0-1 days to 13.0-19.6% at 14-28 days, then decreased to 6.8-11.3% at 42 days and were 2.1-3.8% at 84 days. Nonextractable [^{14}C]residues in the ditch sediment increased from 0.5-1.2% of the applied at 0-1 days to 13.1-13.9% at 42 days and were 9.2-12.7% at 84 days, while in the river sediment increased from 0.3-0.6% at 0-1 days to 18.1-26.3% at 42 days and were 21.3-32.3% at 84 days. Formation of $^{14}CO_2$ (volatilized and water-soluble) totaled 56.3-56.9% and 68.4-68.7% of the applied radioactivity for the ditch and river water-sediment systems, respectively, at study termination. Volatile [^{14}C]organic compounds totaled ≤0.1% of the applied at any sampling interval for both systems.

A transformation pathway was not proposed by the study authors. In this study, MCPA degraded to two unidentified minor nonvolatile products detected in sediment extracts, with significant formation of CO_2.

Results Synopsis:

Test system used: TNO ditch water-sediment from The Netherlands.

Half-life (0- to 84-day data) in water:	12.3 days (r^2 = 0.857).
Half-life (14- to 84-day data) in sediment:	25.5 days (r^2 = 0.956).
Half-life (0- to 84-day data) in total system:	16.3 days (r^2 = 0.905).

Test system used: Kromme Rijn river water-sediment from The Netherlands.

Half-life (0- to 84-day data) in water:	12.3 days (r^2 = 0.879).
Half-life (14- to 84-day data) in sediment:	35.3 days (r^2 = 0.517).
Half-life (0- to 84-day data) in total system:	16.8 days (r^2 = 0.842).

Both systems:

Major transformation products:	None. CO_2.
Minor transformation products:	Two unidentified minor (<10% of applied) [^{14}C]compounds.

Study Acceptability: This study provides marginally acceptable information on the aerobic aquatic metabolism of MCPA. Major deficiencies noted in the study include the fact that both systems represent stratified systems with an aerobic aqueous phase and an anaerobic sediment phase which limits interpretation of the data, the sampling intervals were inadequate to accurately establish the degradation half-life of MCPA, and material balances for the TNO systems were incomplete. However, it is unlikely that repeating this study will result in different results and therefore additional data is not requested at this time.

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I. MATERIALS AND METHODS

GUIDELINE FOLLOWED: This study was conducted in accordance with SETAC-Europe and Draft OECD 308 guidelines as specified by EU Commission Directive 95/36/EC (pp. 4, 10). The following deviations from USEPA Subdivision N Guideline §162-4 were noted:

For both systems, the experimental design employed was inadequate to assess aerobic aquatic degradation because both systems represent stratified systems. The aqueous phase demonstrates aerobic conditions while the sediment phase in both systems demonstrate anaerobic conditions. In addition, sediment redox readings were not recorded after application of the test substance and therefore, the continued anaerobic nature of the system cannot be confirmed. This deficiency limits the interpretation of the study results when applying the results quantitatively.

For both systems, the sampling intervals were inadequate to accurately establish the degradation half-life of MCPA; >50% of the applied [^{14}C]MCPA dissipated between the 14- and 28-day sampling intervals. This affects the validity of the study.

For the TNO systems, material balances were incomplete; 26.8-30.7% of the applied was unaccounted for at study termination. This affects the validity of this portion of the study.

The test waters were not completely characterized. This does not affect the validity of the study.

The test sediments used in this study were not characterized. This does not affect the validity of the study.

Reported physico-chemical properties of MCPA were incomplete. This does not affect the validity of the study.

The test substance may have been applied at significantly less than the maximum application rate, which could affect

	identification of possible degradates of MCPA. This does not affect the validity of the study. The pattern of formation and decline of degradates may not have been adequately addressed; one minor unidentified [^{14}C]comound may have been lost from sediment extracts during concentration steps. This does not affect the validity of the study.
COMPLIANCE:	This study was conducted in compliance with OECD Principles of GLP, (ENV/MC/CHEM(98)17; pp. 3-4, 10). Signed and dated Data Confidentiality, GLP and Quality Assurance statements were provided (pp. 2-3, 9). A Certificate of Authenticity was not provided.
A. MATERIALS:	
1. Test Materials:	[Phenyl-U-^{14}C]-labeled and unlabeled 4-chloro-2-methylphenoxy acetic acid (MCPA; p. 12; Annex A1, p. 35).
Chemical Structure:	See Attachment 2.
Description:	Technical, off-white, coarse powder (p. 12; Annex A1, p. 35).
Purity:	
Radiolabeled:	Radiochemical purity: ≥98.3% (p. 12; Annex A1, p. 35; Annex B, p. 37). Lot No.: 1313A-6-1. Analytical purity: Not reported. Specific activity: 50.64 mCi/mmol. Location of radiolabel: Uniformly in phenyl ring.
Unlabeled:	Analytical purity: 99.9% (p. 12; Annex A2, p. 36). Batch No.: GHP/023/001.
Storage conditions of test chemicals:	Radiolabled MCPA was stored at <-18°C (p. 12). Non-radiolabeled MCPA was stored at room temperature.

Table 1: Physico-chemical properties of MCPA.

Parameter	Values	Comments
Molecular weight:	200 g/mol	
Molecular formula:	$C_9H_9ClO_3$	
Water solubility:	825 mg/L	At 25°C.
Melting point:	118-119°C	
Vapor pressure/volatility:	1.5×10^{-9} mmHg	
UV absorption:	230 nm	
pK_a:	Not reported.	
K_{ow}/log K_{ow}:	Not reported.	
log P_{ow}:	3.3	
Stability of compound at room temperature:	Not reported.	

Data were obtained from Annex A1, p. 35 of the study report; and from
http://ace.ace.orst.edu/info/extoxnet/pips/MCPA.htm and
http://www.ilo.org/public/english/protection/safework/cis/products/icsc/dtasht/_icsc00/icsc0054.pdf.

2. Water-sediment collection, storage and properties:

Table 2: Description of water-sediment collection and storage.

Description		TNO	Kromme Rijn
Geographic location:		North-eastern area of the ditch that surrounds TNO premises, Delft, The Netherlands.	River Kromme Rijn near Odijk, The Netherlands.
Pesticide use history at the collection site:		Not reported.	
Collection date:		April 17, 2002.	April 18, 2002.
		Additional water and sediment collected from both sites on May 7, 2002.	
Collection procedures:	Water:	Not reported.	
	Sediment:	Not reported.	
Sampling depth:	Water:	Not reported.	
	Sediment:	Sampled from 2-3 cm top layer in water at *ca.* 30 cm depth.	
Storage conditions:		Refrigerated (temperature not specified) until use; storage conditions not further described.	

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Description		TNO	Kromme Rijn
Storage length:		Not reported.	
Preparation:	Water:	0.1-mm sieved.	
	Sediment:	2-mm sieved just prior to use.	

Data obtained from p. 13 of the study report.

Table 3: Properties of the waters.

Property		TNO	Kromme Rijn
Temperature (°C)[1]:		12.7	10.3
pH[1]:		8.3	8.0
Redox potential (mV):		Not determined.	
Oxygen concentration (mg/L)[1]:	Surface:	9.9	10.4
	Above sediment:	9.5	10.0
Dissolved organic carbon (mg/L)[2]:		23.9	4.8
Hardness (mg eq. $CaCO_3$/L)[2]:		279.0	219.0
Electrical conductivity:		Not determined.	
Biomass (mg microbial C/100 g, CFU or other):		Not reported.	

[1]Temperature, pH and oxygen content of the waters were measured at the respective site upon collection. The test waters used in this study were not further analyzed (Study Deficiencies No. 4).
[2]This measurement was determined using water samples collected on July 5, 2002, from the same locations, but not used in this study (Annex L, p. 76).
Data obtained from Annex C, p. 38 of the study report.

Table 4: Properties of the sediments[1] .

Property		TNO	Kromme Rijn
Textural classification:		Not reported.	Not reported.
% sand (2000-63 µm):		60.14	27.28
% silt (63-2 µm):		18.39	41.56
% clay (<2 µm):		21.47	31.15
pH (1:5):	In water:	7.9	8.0
	In 1M KCl:	7.5	7.8
	In 0.01M $CaCl_2$	7.5	7.6
Organic carbon (%):		14.9	4.9

Property	TNO	Kromme Rijn
CEC (meq/100 g):	51.8	28.9
Redox potential (mV):	Not determined.	
Bulk density (disturbed, g/cm^3):	Not reported.	
Biomass (mg microbial C/100 g, CFU or other):	Not determined.	

[1]The test sediments used in this study were not characterized. The results presented in this table are from analyses of sediment samples collected on July 5, 2002, from the same locations as the original sediments, but not used in this study (Annex L, p. 76; Study Deficiencies No. 5).
Data obtained from p. 15; Annex C, p. 38 of the study report.

B. EXPERIMENTAL CONDITIONS:

1. Preliminary experiments: A preliminary experiment was conducted to evaluate the extraction and analysis procedures and to estimate the degradation rate of MCPA under aerobic aquatic conditions (p. 15). For each water-sediment type, sediment (amount not specified) was transferred to one bottle and two flasks (Figure 1, p. 14), then flooded with 500 mL of the respective water and pre-incubated as described below. To serve as day 0 samples and evaluate the extraction method, one bottle of each water-sediment type was taken, the water layer was removed (method not specified), and the remaining sediment was treated with *ca.* 0.2 mg [phenyl-U-^{14}C]MCPA (50 µL of 4.6 mg/mL test solution, Reviewer's Comment No. 2). The treated sediments were shaken (method not specified) for 5 minutes, centrifuged (3,000 rpm, 10 minutes), then extracted four times with *ca.* 100-200 mL acetone:0.1M HCl (9:1, v:v; p. 15; Table 1, p. 20). To estimate the degradation rate, the remaining two flasks of each water-sediment system were taken and [^{14}C]MCPA (100 µL of 4.6 mg/mL test solution) was added at *ca.* 0.9 mg/L to the water layers, the treated systems were incubated for 4 and 7 days, then taken and extracted as described below.

For the day 0 sediment samples that were treated and extracted, 86.1% and 80.3% of the applied radioactivity was extractable from the TNO and Kromme Rijn sediments, respectively (Table 1, p. 20).

For both systems at 4 days posttreatment, 99.5-111.8%, 4.1-4.3% and 1.5% of the applied radioactivity was recovered in the water layers, sediment extracts and as $^{14}CO_2$, respectively, with material balances of 108.8-121.7% of the applied (Table 2, p. 20). At 7 days posttreatment, 74.6-83.9%, 5.3-9.0%, 0.8-1.5% and 1.9-2.1% of the applied was recovered in the water layers, sediment extracts, extracted sediments and as $^{14}CO_2$, respectively, with material balances of 87.6-95.3% of the applied.

2. Experimental conditions:

Table 5: Study design.

Parameter		TNO	Kromme Rijn
Duration of the test:		84 days.	
Water: Filtered/unfiltered water: Type and size of filter used, if any:		Filtered. 0.1-mm pore filter.	
Amount of sediment and water/treatment:	Water:	560 g total (160 g associated with sediment + 400 mL water added).	572 g total (172 g associated with sediment + 400 mL water added).
	Sediment:	140 g dry wt (300 g wet wt.).	128 g dry wt. (300 g wet wt.).
Water/sediment ratio:		4:1 (560 g water:140 g dry wt. sediment).	*ca.* 4.5:1 (572 g water:128 g dry wt. sediment).
Nominal application rate (mg a.i./L):		*ca.* 0.8 mg a.i./L (Reviewer's Comment No. 2).	
Actual application rates:		0.74 mg a.i./L (Reviewer's Comment No. 3).	0.72 mg a.i./L.
Control conditions, if used:		No controls were used.	
No. of Replications:	Controls, if used:	No controls were used.	
	Treatments:	Sixteen pre-incubated water-sediment systems were treated with [^{14}C]MCPA.	
Test apparatus (Type/material/volume):		Water-sediment systems contained in 1-L bottles (day 0) or 1-L flasks (all remaining systems) were maintained on a rotary shaker (*ca.* 50 rpm) at room temperature (*ca.* 20°C) in darkness for 19 days prior to treatment.	
Details of traps for CO_2 and organic volatiles, if any:		Each flask (all systems, except day 0) was fitted with a trapping tower layered from bottom to top with oil-covered quartz wool/sponge, soda lime, quartz wool, soda lime and quartz wool; amount/depth of each layer was not specified.	
If no traps were used, is the system closed/open?		Trapping tower was oxygen permeable.	
Identity and concentration of co-solvent:		Methanol, final concentration 0.02% based on water layer (100 µL methanol in 560-572 mL water.	
Test material application:	Volume of test solution used/treatment:	100 µL	
	Application method:	Test solution applied to the water layer; application not further described.	

Parameter		TNO	Kromme Rijn
Any indication of the test material adsorbing to the walls of the test apparatus?		Not reported.	
Biomass (mg microbial C/100 g, CFU or other) of controls:		Initial:	Final:
		Controls were not used.	
Biomass (mg microbial C/100 g, CFU or other) of treated:		Initial:	Final:
		Not determined.	
Experimental conditions:	Temperature (°C):	Room temperature (*ca.* 20°C).	
	Continuous darkness (Yes/No):	Yes.	
Other details, if any:		None.	

Data obtained from pp. 10, 13-16; Figure 1, p. 14; Annex G, p. 42 of the study report.

3. Aerobic conditions: Dissolved oxygen and redox potential of the water layer and redox potential of the sediment were measured every 2-4 days during pre-incubation (Annex E, p. 40). Following treatment, dissolved oxygen and pH of the water layer were measured at 7, 14, 28, 42 and 84 days (Annex F, p. 41). In TNO water-sediment systems after 19 days of pre-incubation, dissolved oxygen and redox potentials in the water layers were 5.9-6.8 mg/L and +138 to +142 mV, respectively, and redox potentials in the sediment were -471 to -405 mV (Annex E, p. 40). In Kromme Rijn water-sediment systems after 19 days of pre-incubation, dissolved oxygen and redox potentials in the water layers were 5.6-5.8 mg/L and +133 to +145 mV, respectively, and redox potentials in the sediment were -543 to -424 mV.

4. Supplementary experiments: None.

5. Sampling:

Table 6: Sampling details.

Criteria	Both systems
Sampling intervals:	0, 1, 3, 7, 14, 28, 42 and 84 days.
Sampling method:	Duplicate treated systems were collected at each interval.
Method of collection of CO_2 and volatile organic compounds:	Upon collection (excluding day 0 systems), the headspace of each system was purged (rate and time interval not specified) with nitrogen to evacuate volatiles through the trapping tower.
Sampling intervals/times for: Sterility check, if sterile controls are used: Dissolved oxygen and pH of water layer:	 Controls were not used. Measured at 7, 14, 28, 42 and 84 days posttreatment.
Sample storage before analysis:	Water and sediment were separated and processed upon sampling. Water layers were analyzed for total radioactivity the day of sampling, then stored frozen (temperature not specified) until HPLC analysis. Sediment samples were extracted upon sampling; however, it was not specified if sediment extracts were analyzed directly or stored prior to analysis.
Other observations, if any:	None.

Data obtained from pp. 16-17; Annex F, p. 41 of the study report.

C. ANALYTICAL METHODS:

Separation of the sediment and water: Prior to separation, an aliquot (10 mL) of the water layer was taken for determination of dissolved $^{14}CO_2$ (p. 16). Then the water layer was decanted and filtered through cotton wool (p. 16).

Extraction/clean up/concentration methods: Aliquots of the water layer were analyzed directly for total radioactivity by LSC (1 mL x 2) and HPLC (100 µL, pp. 16-17).

Sediment was transferred to a plastic centrifuge tube, then extracted one to four times with acetone:0.1M HCl (9:1, v:v); extraction solvent volumes were 100 mL (pp. 16-17; Annex G, pp. 45-47). For each extraction, sediment and extract were shaken for 5 minutes, sediment and extract were separated by centrifugation (>3,000 rpm, *ca.* 10 minutes), then the extract was decanted and filtered through cotton wool. Aliquots (1 mL x 2) of each extract were analyzed for total radioactivity. Extracts were combined, then a sub-sample (volume not specified) of the pooled extract was taken and the acetone removed by rotary evaporation (200 mBar, 80°C). Methanol (volume not specified) was added to the remaining aqueous residue, the sample was centrifuged and an aliquot (100 µL) analyzed by HPLC.

Nonextractable residue determination: Extracted sediment was dried room temperature, ground, then aliquots (*ca.* 50-100 mg x 3) were analyzed for total radioactivity by LSC following combustion (p. 17).

The cotton wool plugs used to filter the water layers were dried at room temperature, then analyzed for total radioactivity by LSC following combustion (p. 17).

Volatile residue determination: The paraffin oil-covered quartz wool/sponge (Reviewer's Comment No. 6.ii) from the volatiles trap was analyzed directly in Ultima Gold scintillation solution for total radioactivity (p. 16).

The soda lime from the volatiles trap was dissolved in 18% HCl, then released $^{14}CO_2$ was purged via nitrogen (flow rate not specified) through Carbosorb:Permafluor cocktail (4:5, v:v) and quantified using LSC (p. 16).

To quantify any $^{14}CO_2$ dissolved in the water layer, an aliquot (10 mL) of the water layer was placed in a biometer flask containing an open vial of 1.5M KOH (2 mL, p. 16). The biometer flask was sealed and 18% HCl solution was injected through a septum into the water sample. The sample was allowed to sit overnight, then released $^{14}CO_2$ trapped in the KOH solution was quantified by LSC.

Total ^{14}C measurement: Total ^{14}C residues were determined by summing the concentrations of residues measured in the water layer, sediment extracts, extracted sediment, and volatile trapping materials (Tables 3-4, p. 21).

Derivatization method, if used: A derivatization method was not employed.

Identification and quantification of parent compound: Water layers and sediment extracts were analyzed by reverse-phase HPLC under the following conditions: Chrompack Chromosorb Hypersil 5 ODS C18 column (4.6 x 250 mm, particle size not reported), isocratic mobile phase of water:acetonitrile:acetic acid (50:50:0.1, v:v), injection volume 100 µL, flow rate 1.0 mL/minute, UV-VIS detector set at 254 or 220 nm, Packard Radiomatic 500TR Flow detector with scintillation fluid flow rate of 3.0 mL/minute (p. 17; Annex, I, pp. 60-66). Radiograms were constructed following fraction collection (1-minute intervals) and LSC analysis (p. 15). [^{14}C]MCPA was identified by comparison to the retention time of unlabeled reference standard (p. 17).

Selected sediment extracts were also analyzed using one-dimensional TLC on silica gel plates (Merck 60F254, thickness not specified) developed with hexane:diethyl ether (1:1, v:v; p. 17). Following development, areas of radioactivity were detected using a Bioscan TLC-radiometer. [^{14}C]MCPA was identified by comparison to the R_f value of labeled reference standard (Annex J, pp. 67-69).

Identification and quantification of transformation products: Transformation products were separated and quantified by HPLC as described for parent MCPA.

Detection limits (LOD, LOQ) for the parent compound and transformation products: Limits of detection (LOD) and quantitation (LOQ) for the LSC and HPLC analyses were not reported.

II. RESULTS AND DISCUSSION:

A. TEST CONDITIONS: Redox potentials in the water layers and sediments were not measured following treatment. During the 84-day incubation, dissolved oxygen and pH were 1.4-4.7 mg/L and 7.6-8.6, respectively, in the TNO water layers and 1.5-5.4 mg/L and 7.4-8.2, respectively, in the Kromme Rijn water layers (Annex F, p. 41).

B. MATERIAL BALANCE: In TNO water-sediment systems, recovery of radiolabeled material averaged 88.7 ± 13.0% (range 69.3-116.6%, n = 16) of the applied, with material balances declining from 89.0-116.6% at 0-3 days posttreatment to 69.3-73.2% at 84 days (Table 3, p. 21; Attachment 1). Following application of [^{14}C]MCPA to the water layer, [^{14}C]residues partitioned into the sediment with mean distribution ratios (water:sediment, n = 2) of 62-69:1 at 0-1 days, 27:1 at 3 days, 6:1 at 7 days, 3:1 at 14 days, 1:5-6 at 28-42 days and 1:9 at 84 days (Attachment 1).

In Kromme Rijn water-sediment systems, recovery of radiolabeled material averaged 100.1 ± 9.0% (range 82.0-117.6%, n = 16) of the applied, with no consistent decline in material balances during the 84-day study (Table 4, p. 21; Attachment 1). Following application of [^{14}C]MCPA to the water layer, [^{14}C]residues partitioned into the sediment with mean distribution ratios (water:sediment) of 113-153:1 at 0-1 days, 15:1 at 3 days, 7:1 at 7 days, 3:1 at 14 days, 1:6-7 at 28-42 days and 1:23 at 84 days (Attachment 1).

Table 7: Biotransformation of [phenyl-U-^{14}C]MCPA, expressed as percentage of applied radioactivity (mean ± s.d., n = 2), in TNO ditch water-sediment under aerobic conditions.

Compound		Sampling times (days)							
		0	1	3	7	14	28	42	84
MCPA HPLC R_t = 5.7 min. (p. 25).	water	91.1 ± 3.1	88.0 ± 1.0	110.8 ± 0.1	77.6 ± 2.7	61.2 ± 5.5	6.5 ± 3.6	4.4 ± 0.5	1.4 ± 0.1
	sediment	1.0 ± 0.5	0.7 ± 0.1	2.7 ± 0.1	8.4 ± 0.7	17.6 ± 1.7	8.5 ± 0.8	7.0 ± 0.2	2.4 ± 0.2
	system[1]	92.1 ± 3.6	88.7 ± 1.1	113.6 ± 0.0	86.0 ± 3.5	78.9 ± 3.8	15.0 ± 4.4	11.5 ± 0.3	3.7 ± 0.2
Unknown Metabolite 1 HPLC R_t = 4.5 min.	water	–[2]	--	--	--	--	--	--	--
	sediment	--	--	--	--	--	2.8 ± 1.5	--	--
	system	--	--	--	--	--	2.8 ± 1.5	--	--
Unknown Metabolite 2 HPLC R_t = 6.7 min.	water	--	--	--	--	--	--	--	--
	sediment	--	--	--	--	--	5.0 ± 1.0	--	--
	system	--	--	--	--	--	5.0 ± 1.0	--	--
Nonextractable sediment residues		0.8 ± 0.3	0.6 ± 0.1	1.4 ± 0.0	3.8 ± 0.8	6.9 ± 2.1	10.2 ± 1.2	13.5 ± 0.4	10.9 ± 1.8
CO_2	in water layer	n.d.[3]	1.2 ± 0.0	1.1 ± 0.2	1.0 ± 0.2	1.9 ± 0.1	30.6 ± 2.3	16.6 ± 1.8	4.5 ± 1.2
	volatile		0.2 ± 0.1	0.4 ± 0.1	0.7 ± 0.0	1.3 ± 0.2	16.0 ± 1.4	36.5 ± 1.0	52.0 ± 1.5
	entire system		1.4 ± 0.1	1.5 ± 0.1	1.8 ± 0.2	3.1 ± 0.0	46.7 ± 3.7	53.1 ± 0.8	56.6 ± 0.3
Total volatile organics		n.d.	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total % recovery	water	91.1 ± 3.1	88.1 ± 1.0[4]	110.8 ± 0.1	77.6 ± 2.7	61.2 ± 5.5	6.5 ± 3.7	4.4 ± 0.5	1.4 ± 0.1
	sediment	1.8 ± 0.9	1.3 ± 0.2	4.2 ± 0.1	12.1 ± 1.5	24.5 ± 3.7	26.5 ± 2.1	20.6 ± 0.6	13.3 ± 1.6
	system	93.0 ± 4.0	90.8 ± 1.3	116.5 ± 0.1	91.5 ± 4.4	88.9 ± 1.7	79.6 ± 2.1	78.1 ± 0.7	71.3 ± 2.0

[1]Entire system; water + sediment.

[2]Not detected; radioactivity equivalent to background (p. 25).

[3]Not determined.

[4]Reviewer's Comment No. 6.iv.

Data obtained from Table 3, p. 21; Tables 5-7, pp. 24-26; Tables H1-H2, p. 55 of the study report and Attachment 1.

Table 8: Biotransformation of [phenyl-U-^{14}C]MCPA, expressed as percentage of applied radioactivity (mean ± s.d., n = 2), in Kromme Rijn river water-sediment under aerobic conditions.

Compound		Sampling times (days)							
		0	1	3	7	14	28	42	84
MCPA HPLC R_t = 5.7 min.	water	95.4 ± 6.4	102.0 ± 0.3	102.8 ± 8.0	90.7 ± 1.5	66.8 ± 1.1	6.2 ± 1.0	5.0 ± 0.4	1.5 ± 0.4
	sediment	0.3 ± 0.0	0.4 ± 0.1	5.5 ± 2.5	9.3 ± 0.5	17.6 ± 0.2	8.3 ± 1.3	2.9 ± 0.1	3.8 ± 0.0
	system[1]	95.7 ± 6.3	102.3 ± 0.3	108.3 ± 5.5	100.1 ± 1.0	84.4 ± 0.9	14.5 ± 0.3	7.9 ± 0.6	5.3 ± 0.5
Unknown Metabolite 1 HPLC R_t = 4.5 min.	water	–[2]	--	--	--	--	--	--	--
	sediment	--	--	--	--	--	--	2.8 ± 0.2	--
	system	--	--	--	--	--	--	2.8 ± 0.2	--
Unknown Metabolite 2 HPLC R_t = 6.7 min.	water	--	--	--	--	--	--	--	--
	sediment	--	--	--	--	--	9.1 ± 0.2	4.9 ± 0.3	--
	system	--	--	--	--	--	9.1 ± 0.2	4.9 ± 0.3	--
Nonextractable sediment residues		0.4 ± 0.0	0.6 ± 0.1	3.5 ± 1.6	3.6 ± 0.8	7.6 ± 0.3	16.9 ± 0.3	22.2 ± 4.1	26.8 ± 5.5
CO_2	in water layer	n.d.[3]	1.7 ± 0.1	1.5 ± 0.1	1.1 ± 0.1	1.9 ± 0.2	27.8 ± 2.3	15.9 ± 0.1	3.1 ± 1.1
	volatile		0.2 ± 0.0	0.3 ± 0.0	0.8 ± 0.1	1.8 ± 0.1	15.0 ± 1.0	47.3 ± 0.1	65.4 ± 1.2
	entire system		1.8 ± 0.1	1.8 ± 0.1	1.9 ± 0.0	3.7 ± 0.1	42.8 ± 1.4	63.2 ± 0.3	68.5 ± 0.1
Total volatile organics		n.d.	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Total % recovery	water	95.4 ± 6.4	102.0 ± 0.3	102.8 ± 8.0	90.8 ± 1.5	66.8 ± 1.1	6.2 ± 1.0	5.0 ± 0.4	1.5 ± 0.4
	sediment	0.6 ± 0.0	0.9 ± 0.0	9.0 ± 4.0	13.0 ± 1.4	25.2 ± 0.1	34.3 ± 1.1	32.8 ± 3.4	30.6 ± 5.5
	system	96.0 ± 6.4	104.8 ± 0.5	113.6 ± 4.0	105.6 ± 0.2	95.7 ± 1.3	83.3 ± 1.3	101.0 ± 2.7	100.7 ± 5.2

[1]Entire system; water + sediment.

[2]Not detected; radioactivity equivalent to background (p. 25).

[3]Not determined.

Data obtained from Table 4, p. 21; Tables 8-10, pp. 27-28; Tables H3-H4, p. 58 of the study report and Attachment 1.

[2]Data obtained from Tables 11-21, pp. 29-30 of the study report.
[3]Not determined.

TRANSFORMATION PRODUCTS: No major nonvolatile transformation products of MCPA were detected. Two minor products (HPLC R_t = 4.5 and 6.7 minutes) were detected in sediment extracts, but not identified. In TNO sediment, the unidentified [^{14}C]compounds of HPLC R_t = 4.5 and 6.7 minutes were detected at 1.2-4.3% and 4.0-5.9% of the applied, respectively, at 28 days only and were not detected at any other interval (Table H1, p. 55). In Kromme Rijn sediment, the [^{14}C]compound of HPLC R_t = 4.5 minutes was only detected at 2.6-3.0% of the applied at 42 days, while the compound of HPLC R_t of 6.7 minutes was detected at 8.9-9.3% at 28 days, 4.6-5.2% at 42 days and was not detected at any other interval (Table H3, p. 58).

NONEXTRACTABLE AND EXTRACTABLE RESIDUES: For TNO sediment, extractable [^{14}C]residues increased from 0.46-1.54% of the applied at 0-1 days to 12.96-19.61% at 14-28 days, then decreased to 6.82-7.25% at 42 days and were 2.14-2.58% at 84 days (Table G4, p. 45). Nonextractable [^{14}C]residues increased from 0.52-1.18% at 0-1 days to 13.13-13.92% at 42 days and were 9.16-12.74% at 84 days (Table G5, pp. 48-51; Attachment 1).

For Kromme Rijn sediment, extractable [^{14}C]residues increased from 0.26-0.27% of the applied at day 0 to 16.00-18.86% at 14-28 days, then decreased to 9.89-11.30% at 42 days and were 3.75-3.79% at 84 days (Table G4, p. 45). Nonextractable [^{14}C]residues increased from 0.35-0.37% at day 0 to 18.09-26.28% at 42 days and were 21.34-32.28% at 84 days (Table G5, pp. 48-51; Attachment 1).

VOLATILIZATION: Formation $^{14}CO_2$ (volatilized and water-soluble) was significant for both systems totaling 56.3-56.9% and 68.4-68.7% of the applied radioactivity for the TNO and Kromme Rijn systems, respectively, at study termination (Table G2, p. 42; Table G3, p. 44; Table G6, p. 52; Attachment 1). Volatile [^{14}C]organic compounds totaled ≤0.1% of the applied at any sampling interval for both systems (Tables 3-4, p. 21).

TRANSFORMATION PATHWAY: A transformation pathway was not proposed by the study authors. In this study, MCPA degraded to two unidentified minor nonvolatile products, with significant formation of CO_2.

Table 10: Chemical names for identified transformation products of MCPA in aerobic water-sediment.

Applicant's code	CAS Number	Chemical Name(s)	Chemical formula	Molecular weight	SMILES string

D. SUPPLEMENTARY EXPERIMENT-RESULTS: None.

III. STUDY DEFICIENCIES: This study cannot be used to fulfill the aerobic aquatic metabolism guideline, Subdivision N Guideline §162-4, data requirements for MCPA for the following reasons:

1. For both systems, the sediment was not flooded and treated at the same time. For an aerobic aquatic metabolism study, an aerobic soil/sediment should be treated and flooded at the same time so that both aerobic and anaerobic conditions exist in the soil/sediment and the initial microbial population of the soil/sediment is predominantly aerobic. In this study after 19 days of pre-incubation and prior to treatment, dissolved oxygen and redox potentials in the water layers of both systems were 5.6-6.8 mg/L and +133 to +145 mV, respectively, and redox potentials in the sediment were -543 to -405 mV (Annex E, p. 40).

2. For both systems, the sampling intervals were inadequate to accurately establish the degradation half-life of MCPA. Between the 14- and 28-day sampling intervals, [^{14}C]MCPA decreased from 75.1-82.7% of the applied to 10.5-19.3% in the TNO systems and from 83.6-85.4% to 14.3-14.8% in the Kromme Rijn systems.

3. For the TNO systems, material balances were incomplete decreasing from 89.0-116.6% of the applied at 0-3 days posttreatment to 69.3-73.2% at study termination. The study authors proposed that the low recoveries were due to loss of volatilized $^{14}CO_2$ (p. 22).

Additional study deficiencies include the following:

4. The test waters were not completely characterized. The temperature, pH and oxygen content of the test waters used in this study were measured at the respective site upon collection, but were not further analyzed (p. 13; Table C1, p. 38).

5. The test sediments used in this study were not characterized. The sediment characterizations presented in this study were from analyses of sediment samples collected on July 5, 2002, from the same locations as the original sediments (collected April 17-18 and May 7, 2002) used in this study.

6. Physico-chemical properties of MCPA were incomplete; the aqueous solubility, vapor pressure/volatility, pK_a, K_{ow}/log K_{ow}, and stability at room temperature should have been reported.

7. The test substance may have been applied at significantly less than the maximum application rate, which could affect identification of possible degradates of MCPA. No justification was provided for the selected nominal application rate of 1.0 mg/L water used in this study, and the intended maximum field use rate for MCPA was not reported.

8. The pattern of formation and decline of degradates may not have been adequately addressed. One degradate, unidentified [^{14}C]comound of HPLC R_t = 5.7 minutes was detected at 4.0-9.3% of the applied in non-concentrated sediment extracts at 28-42 days posttreatment. The study authors suggested that this degradate was probably lost from sediment extracts at other intervals during evaporation steps (pp. 26, 28).

IV. REVIEWER'S COMMENTS:

1. Two foreign (Netherlands) sediments were used in this study and characterized according to German BBA soil classification guidelines; however, the textural classifications of the two sediments were not reported by the study authors. The particle size scale ranges differed from those used by the USDA soil classification system. According to German BBA soil classification guidelines, particles in the range of 2.0-0.063 mm are categorized as sand, 0.063-0.002 mm as silt and <0.002 mm as clay.

2. Actual nominal application rate was reported by the study authors to be 1 mg/L (pp. 10, 15); however, the nominal application rate was actually closer to 0.8 mg a.i./L.

   Radioactivity of initial test solution 3,776 kBq/mL = 3.776 x 10^6 Bq/mL.

   1 Ci = 3.7 x 10^{10} Bq = 3.7 x 10^7 Bq/mCi

   (3.776 x 10^6 Bq/mL)/(3.7 x 10^7 Bq/mCi) = 0.102 mCi.

   [^{14}C]MCPA specific activity = 50.64 mCi/mmol (p. 12).

   (0.102 mCi)/(50.64 mCi/mmol) = 0.002015 mmol.

   MCPA molecular weight = 200 g/mole Annex A1, p. 35) = 200 mg/mmol.

   0.002015 mmol x 200 mg/mmol = 0.403 mg [^{14}C]MCPA.

   Added 0.0234 g unlabeled MCPA (p. 15) = 23.4 mg.

   Total MCPA = 0.403 mg [^{14}C]MCPA + 23.4 mg unlabeled MPCA = 23.8 mg.

   In total volume of 5.15 mL methanol (p. 15) = 4.62 mg/mL test concentration.

   Test system dosed with 100 µL or 0.1 mL (p. 15) = 0.46 mg.

   Water phase totals (added water plus water associated with sediment) of 560 mL (TNO) and 572 mL (Kromme Rijn).

Therefore, actual nominal application rates of 0.82 mg/L (TNO) and 0.80 mg/L (Kromme Rijn).

3. Actual application rates were determined as follows:

   Radioactivity of initial test solution 3,776 kBq/mL (p. 15).

   Test systems dosed with 0.1 mL of test solution = 377.6 kBq/mL = 377,600 Bq/mL.

   Initial radioactivity checks during application to day 0 systems = 325,791 Bq/mL to 415,373 Ba/mL (Annex G, p. 42), equivalent to 86.3% to 110.0% of the initial 377,600 Bq/mL.

   And, the average 340,131 Bq/mL = 90.1% of the initial 377,600 Bq/mL.

   Therefore, actual application rates were 0.901 x 0.82 mg/L = 0.74 mg/L for the TNO systems and 0.901 x 0.80 mg/L = 0.72 mg/L for the Kromme Rijn systems.

4. According to N. Wolfe, *et al.* (see reference below), redox potentials in the range of +400 to +800 mV are considered strongly oxidizing, +200 to +400 mV moderately oxidizing, -50 to +200 mV moderately reducing, -200 to -50 mV reducing, and -400 to -200 mV strongly reducing.

5. Limits of detection (LOD) and quantitation (LOQ) for the LSC and HPLC analyses were not reported.

6. The following typographical errors/discrepancies were noted:

   i) In section 2.2.1 Characterisation of water and sediments (p. 13), the study authors reported that redox potential of the test waters was measured upon collection; however, the reported results in Annex C (p. 38) indicate that redox potentials were not determined.

   ii) In Figure 1 (p. 14), the trapping tower materials consisted of oil-covered quartz wool, a sponge, soda lime and unoiled quartz wool; however, in section 2.4 Analytical procedures (p. 16), the study authors reported that a paraffin oil-covered sponge was removed from the trapping tower.

   iii) In section 2.4 Analytical procedures (p. 16), the study authors reported that the sampling intervals were 0, 1, 4, 7, 14, 28, 42, and 84 days; however, the actual sampling intervals were 0, 1, 3, 7, 14, 28, 42, and 84 days.

iv) In section 3.5 Distribution of the radioactivity in the test systems (p. 21), it was stated that measured data and calculated results were presented in Annex H; however, those results were actually presented in Annex G.

v) In Table 3 (p. 21), the study authors reported the mean radioactivity recovered in the "Aqueous phase" value as 88.8% of the applied; however, the individual replicate results were 87.0% and 89.1% (Annex G, p. 43) which yields a mean of 88.1% (Attachment 1).

7. (4-Chloro-2-methylphenoxy)acetic acid and 4-chloro-o-tolyloxyacetic acid were identified as IUPAC names and (4-chloro-2-methylphenoxy)acetic acid was identified as a CAS name of MCPA by the Compendium of Pesticide Common Names (http://www.hclrss.demon.co.uk/mcpa.html). CAS Reg. No. 94-74-6 for MCPA was confirmed by the Compendium of Pesticide Common Names and USEPA/OPP Chemical Database (http://www.cdpr.ca.gov/cgi-bin/epa/chemidetriris.pl?pccode=030501). Synonyms methyl-4-chlorophenoxy acetic acid, CMP acetate, chloro-o-cresoxy acetic acid and metaxon.for MCPA were obtained from the USEPA/OPP Chemical Database.

V. REFERENCES:

1. U.S. Environmental Protection Agency. 1982. Pesticide Assessment Guidelines, Subdivision N, Chemistry: Environmental Fate, Section 162-4, Aerobic Aquatic Metabolism Studies. Office of Pesticide and Toxic Substances, Washington, DC. EPA 540/9-82-021.

2. U.S. Environmental Protection Agency. 1989. FIFRA Accelerated Reregistration, Phase 3 Technical Guidance. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 540/09-90-078.

3. U.S. Environmental Protection Agency. 1993. Pesticide Registration Rejection Rate Analysis - Environmental Fate. Office of the Prevention, Pesticides, and Toxic Substances, Washington, DC. EPA 738-R-93-010.

4. Wolfe, N., *et al.* 1990. Abiotic transformations in water, sediments and soil. *In* Pesticides in the Soil Environment, Soil Science Society of America, pp. 103-110.

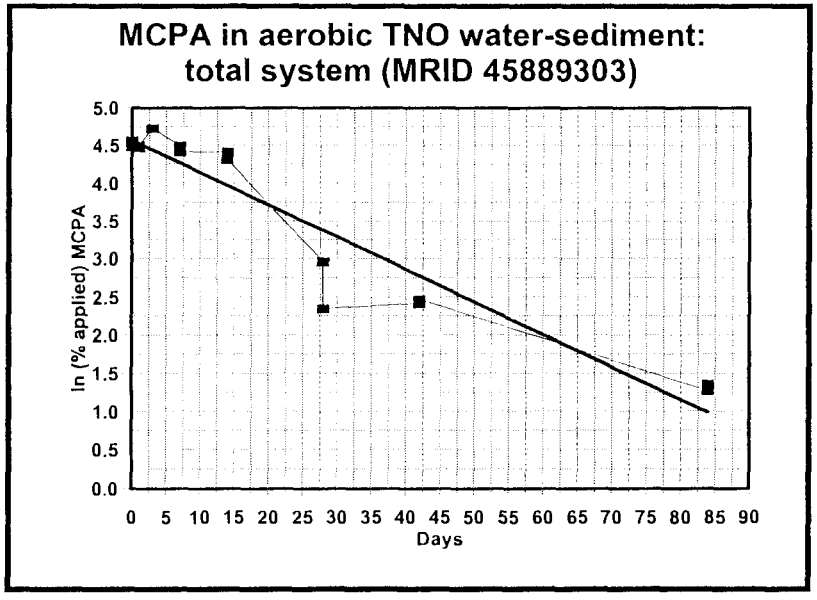
Attachment 1

Quattro Pro Graphs and Spreadsheets

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

TNO Water-Sediment.
Total System.
MCPA
Half-life Determination

Day	MCPA	
	%App	Ln(%App)
0	95.7	4.561218
0	88.5	4.483003
1	87.6	4.472781
1	89.9	4.498698
3	113.5	4.731803
3	113.5	4.731803
7	89.4	4.493121
7	82.5	4.412798
14	82.7	4.41522
14	75.1	4.318821
28	19.3	2.960105
28	10.5	2.351375
42	11.2	2.415914
42	11.8	2.4681
84	3.6	1.280934
84	3.9	1.360977



0- to 84-day data

Regression Output:

Constant	4.58
Std Err of Y Est	0.4
R Squared	0.905
No. of Observations	16
Degrees of Freedom	14
X Coefficient(s)	-0.0426
Std Err of Coef.	0.003696

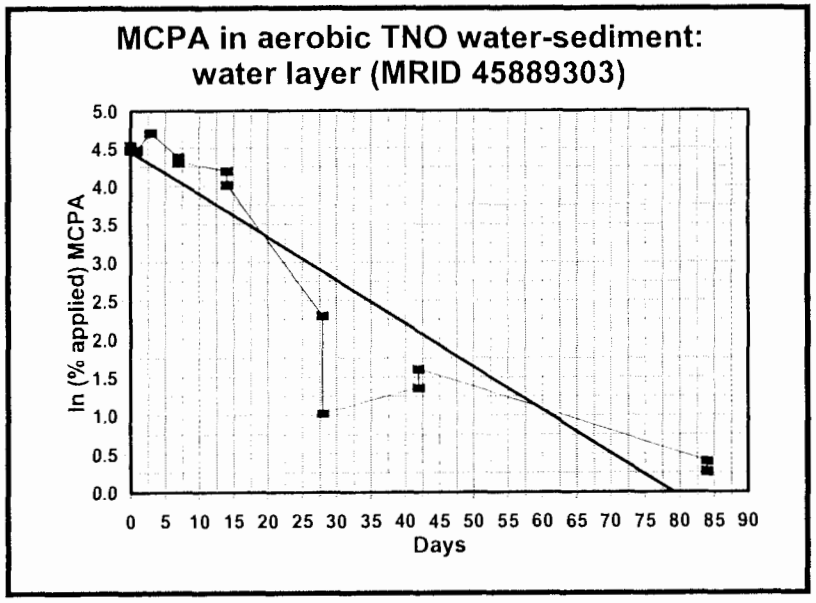
half-life 16.3 days

*AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8.
Results (% of applied radioactivity) from Annex H, p. 55 of the study report.

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

TNO Water-Sediment.
Water layer.
MCPA
Half-life Determination

Day	MCPA	
	%App	Ln(%App
0	94.2	4.54542
0	88.0	4.477337
1	87.0	4.465908
1	89.1	4.489759
3	110.7	4.706824
3	110.9	4.708629
7	80.3	4.38577
7	74.9	4.316154
14	66.7	4.200205
14	55.8	4.021774
28	10.0	2.302585
28	2.8	1.029619
42	3.9	1.360977
42	5.0	1.609438
84	1.5	0.405465
84	1.3	0.262364



0- to 84-day data

Regression Output:

Constant	4.47
Std Err of Y Est	0.667
R Squared	0.857
No. of Observations	16
Degrees of Freedom	14
X Coefficient(s)	-0.0564
Std Err of Coef.	0.00616

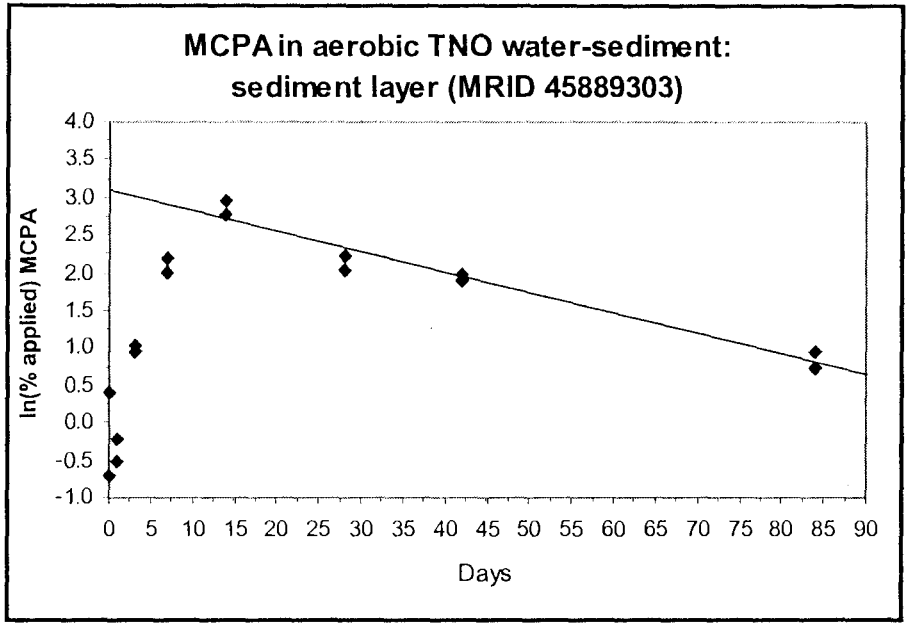
half-life ***12.3 days***

*AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8.
Results (% of applied radioactivity) from Annex H, p. 55 of the study report.

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

TNO Water-Sediment.
Sediment layer.
MCPA
Half-life Determination

Day	MCPA	
	%App	Ln(%App)
0	1.5	0.4054651
0	0.5	-0.693147
1	0.6	-0.510826
1	0.8	-0.223144
3	2.8	1.0296194
3	2.6	0.9555114
7	9.1	2.2082744
7	7.6	2.0281482
14	16.0	2.7725887
14	19.3	2.9601051
28	9.3	2.2300144
28	7.7	2.0412203
42	7.3	1.9878743
42	6.8	1.9169226
84	2.1	0.7419373
84	2.6	0.9555114



14- to 84-day data

Regression Output:

Constant	3.09
Std Err of Y Est	0.177
R Squared	0.956
No. of Observations	8
Degrees of Freedom	6
X Coefficient(s)	-0.0272
Std Err of Coef.	0.002391

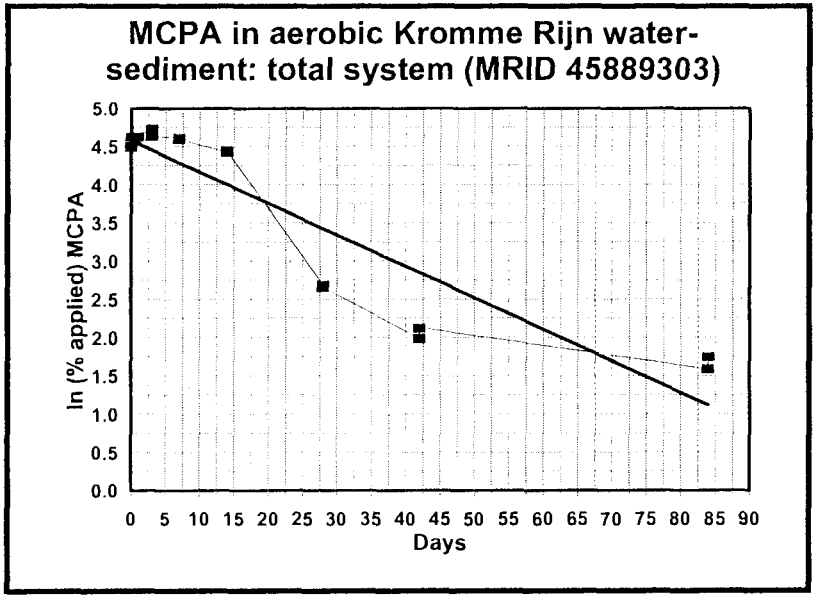
half-life 25.5 days

*AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8.
Results (% of applied radioactivity) from Annex H, p. 55 of the study report.

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

Kromme Rijn Water-Sediment.
Total System.
MCPA
Half-life Determination

Day	MCPA	
	%App	Ln(%App)
0	102.1	4.6259527
0	89.4	4.4931207
1	102.6	4.6308379
1	102.1	4.6259527
3	113.8	4.7344425
3	102.8	4.6327854
7	101.1	4.6161101
7	99.1	4.5961294
14	83.6	4.4260435
14	85.4	4.4473461
28	14.8	2.6946272
28	14.3	2.6602595
42	7.3	1.9878743
42	8.4	2.1282317
84	4.9	1.5892352
84	5.8	1.7578579



0- to 84-day data

Regression Output:

Constant	4.59
Std Err of Y Est	0.515587
R Squared	0.842
No. of Observations	16
Degrees of Freedom	14
X Coefficient(s)	-0.0412
Std Err of Coef.	0.004765

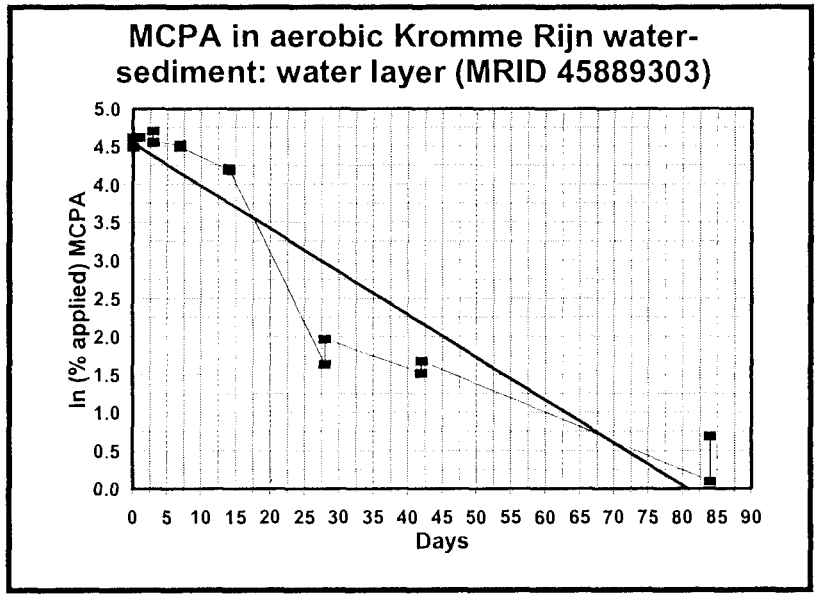
half-life **16.8 days**

*AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8.
Results (% of applied radioactivity) from Annex H, p. 58 of the study report.

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

Kromme Rijn Water-Sediment.
Water layer.
MCPA
Half-life Determination

Day	MCPA	
	%App	Ln(%App)
0	101.8	4.6230101
0	89.1	4.4897593
1	102.3	4.6279097
1	101.7	4.6220273
3	110.8	4.7077268
3	94.9	4.5528237
7	92.3	4.5250441
7	89.2	4.490881
14	65.8	4.1866198
14	67.9	4.218036
28	5.2	1.6486586
28	7.2	1.974081
42	4.6	1.5260563
42	5.4	1.686399
84	1.1	0.0953102
84	2.0	0.6931472



0- to 84-day data

Regression Output:

Constant	4.55
Std Err of Y Est	0.603038
R Squared	0.879
No. of Observations	16
Degrees of Freedom	14
X Coefficient(s)	-0.0562
Std Err of Coef.	0.005573

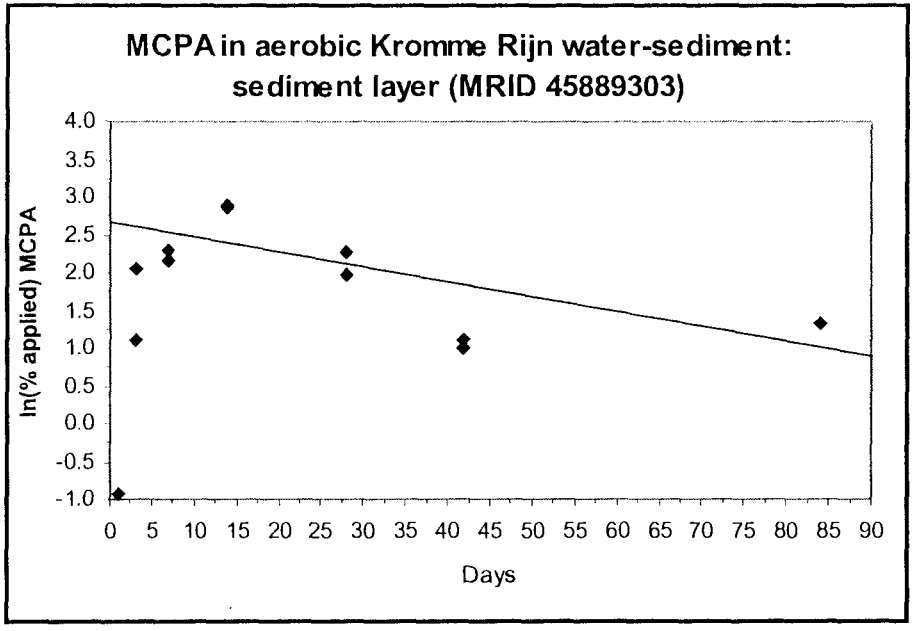
half-life 12.3 days

*AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8.
Results (% of applied radioactivity) from Annex H, p. 58 of the study report.

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

Kromme Rijn Water-Sediment.
Sediment layer.
MCPA
Half-life Determination

Day	MCPA	
	%App	Ln(%App)
0	0.3	-1.203973
0	0.3	-1.203973
1	0.3	-1.203973
1	0.4	-0.916291
3	3.0	1.0986123
3	7.9	2.0668628
7	8.8	2.1747517
7	9.9	2.2925348
14	17.8	2.8791985
14	17.5	2.8622009
28	9.6	2.2617631
28	7.1	1.9600948
42	2.7	0.9932518
42	3.0	1.0986123
84	3.8	1.3350011
84	3.8	1.3350011



14- to 84-day data

Regression Output:

Constant	2.67
Std Err of Y Est	0.574349
R Squared	0.517
No. of Observations	8
Degrees of Freedom	6
X Coefficient(s)	-0.0196
Std Err of Coef.	0.007753

half-life 35.3 days

*AR = Applied Radioactivity
Linear regression analysis performed using Corel Quattro Pro 8.
Results (% of applied radioactivity) from Annex H, p. 58 of the study report.

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

TNO Water-Sediment.
Determination of means/standard deviations for applied radioactivity.

				Sediment														
	Water[1]			Extract[2]			Nonextractable[3]			$^{14}CO_2$ in Water[4]			Volatile $^{14}CO_2$[5]			Material Balance		
Day	% AR	Mean	s.d.	%AR	Mean	s.d.	% AR	Mean	s.d.	% AR	Mean	s.d.	% AR	Mean	s.d.	% AR	Mean	s.d.
0	94.2			1.54			1.18			NA[6]			NA			96.9		
0	88.0	91.1	3.1	0.46	1.0	0.5	0.52	0.8	0.3	NA	0.0	0.0	NA	0.0	0.0	89.0	92.9	4.0
1	87.0			0.58			0.53			1.2			0.1			89.4		
1	89.1	88.1	1.0	0.81	0.7	0.1	0.72	0.6	0.1	1.3	1.2	0.0	0.2	0.2	0.1	92.1	90.8	1.3
3	110.7			2.82			1.43			1.3			0.3			116.6		
3	110.9	110.8	0.1	2.64	2.7	0.1	1.43	1.4	0.0	1.0	1.1	0.2	0.4	0.4	0.1	116.4	116.5	0.1
7	80.3			9.13			4.52			1.2			0.7			95.9		
7	74.9	77.6	2.7	7.61	8.4	0.8	2.99	3.8	0.8	0.9	1.0	0.2	0.7	0.7	0.0	87.1	91.5	4.4
14	66.7			15.99			4.83			2.0			1.1			90.6		
14	55.8	61.3	5.5	19.27	17.6	1.6	8.98	6.9	2.1	1.7	1.9	0.1	1.5	1.3	0.2	87.2	88.9	1.7
28	10.1			19.61			9.01			28.4			14.6			81.7		
28	2.8	6.5	3.7	12.96	16.3	3.3	11.37	10.2	1.2	32.9	30.6	2.3	17.5	16.0	1.4	77.5	79.6	2.1
42	3.9			7.25			13.92			14.7			37.6			77.4		
42	5.0	4.5	0.5	6.82	7.0	0.2	13.13	13.5	0.4	18.4	16.6	1.8	35.5	36.5	1.0	78.8	78.1	0.7
84	1.5			2.14			12.74			3.3			53.6			73.2		
84	1.3	1.4	0.1	2.58	2.4	0.2	9.16	10.9	1.8	5.8	4.5	1.2	50.5	52.0	1.5	69.3	71.3	2.0
																	88.7	13.0

[1]Results (% of applied radioactivity) from Annex G, p. 43 of the study report.
[2]Results (% of applied radioactivity) from Annex G, p. 45 of the study report.
[3]Results (% of applied radioactivity) calculated by primary reviewer using sample radioactivity (in Bq) from Annex G, pp. 48-51 and initial radioactivity applied (in Bq) from Annex G, p. 42 of the study report. Example, TNO 84D A = (50477 Bq/396290 Bq)*100 = 12.74% of appli
[4]Results (% of applied radioactivity) calculated by primary reviewer using sample radioactivity (in Bq) from Annex G, p. 44 and initial radioactivity applied (in Bq) from Annex G, p. 42 of the study report.
[5]Results (% of applied radioactivity) calculated by primary reviewer using sample radioactivity (in Bq) from Annex G, p. 52 and initial radioactivity applied (in Bq) from Annex G, p. 42 of the study report.
[6]Not analyzed.
Means and standard deviations calculated using Corel Quattro Pro 8 program functions @avg(A1..A2) and @std(A1..A2).

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

TNO Water-Sediment.
Determination of total radioactivity associated with sediment.

	Sediment				
	Ext	Nonext	Total		
Day	%AR	% AR	% AR	Mean	s.d.
0	1.54	1.18	2.7		
0	0.46	0.52	1.0	1.8	0.9
1	0.58	0.53	1.1		
1	0.81	0.72	1.5	1.3	0.2
3	2.82	1.43	4.2		
3	2.64	1.43	4.1	4.2	0.1
7	9.13	4.52	13.7		
7	7.61	2.99	10.6	12.1	1.5
14	15.99	4.83	20.8		
14	19.27	8.98	28.3	24.5	3.7
28	19.61	9.01	28.6		
28	12.96	11.37	24.3	26.5	2.1
42	7.25	13.92	21.2		
42	6.82	13.13	19.9	20.6	0.6
84	2.14	12.74	14.9		
84	2.58	9.16	11.7	13.3	1.6

[14C]Residue water phase:sediment ratios.

	Water	Sed	Ratio	Ratio	Mean	s.d.	Mean	s.d.
Day	% AR	% AR	W:S	S:W	W:S ratio		S:W ratio	
0	94.2	2.7	35	0				
0	88.0	1.0	90	0	62	28	0	0
1	87.0	1.1	79	0				
1	89.1	1.5	58	0	69	10	0	0
3	110.7	4.2	26	0				
3	110.9	4.1	27	0	27	1	0	0
7	80.3	13.7	6	0				
7	74.9	10.6	7	0	6	1	0	0
14	66.7	20.8	3	0				
14	55.8	28.3	2	1	3	1	0	0
28	10.1	28.6	0	3				
28	2.8	24.3	0	9	0	0	6	3
42	3.9	21.2	0	5				
42	5.0	19.9	0	4	0	0	5	1
84	1.5	14.9	0	10				
84	1.3	11.7	0	9	0	0	9	0

Results (% of applied radioactivity) from Annex G, pp. 43, 45 of the study report and calculated results (% of applied) using sa radioactivity results (in Bq) from Annex G, pp. 42, 48-51.
Means and standard deviations calculated using Corel Quattro Pro 8 program functions @avg(A1..A2) and @std(A1..A2).

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

Kromme Rijn Water-Sediment.
Determination of means/standard deviations for applied radioactivity.

				Sediment														
	Water[1]			Extract[2]			Nonextractable[3]			$^{14}CO_2$ in Water[4]			Volatile $^{14}CO_2$[5]			Material Balance		
Day	% AR	Mean	s.d.	%AR	Mean	s.d.	% AR	Mean	s.d.	% AR	Mean	s.d.	% AR	Mean	s.d.	% AR	Mean	s.d.
0	101.8			0.27			0.37			NA[6]			NA			102.4		
0	89.1	95.5	6.4	0.26	0.3	0.0	0.35	0.4	0.0	NA	0.0	0.0	NA	0.0	0.0	89.7	96.1	6.4
1	102.3			0.33			0.62			1.79			0.21			105.3		
1	101.7	102.0	0.3	0.37	0.4	0.0	0.49	0.6	0.1	1.54	1.7	0.1	0.16	0.2	0.0	104.3	104.8	0.5
3	110.8			3.01			1.93			1.61			0.24			117.6		
3	94.9	102.9	8.0	7.92	5.5	2.5	5.07	3.5	1.6	1.39	1.5	0.1	0.30	0.3	0.0	109.6	113.6	4.0
7	92.3			8.79			2.80			1.22			0.70			105.8		
7	89.2	90.8	1.5	9.90	9.3	0.6	4.42	3.6	0.8	1.07	1.1	0.1	0.83	0.8	0.1	105.4	105.6	0.2
14	65.8			17.77			7.32			1.63			1.95			94.5		
14	67.9	66.9	1.1	17.46	17.6	0.2	7.85	7.6	0.3	2.12	1.9	0.2	1.68	1.8	0.1	97.0	95.7	1.3
28	5.2			18.86			16.54			25.51			15.93			82.0		
28	7.2	6.2	1.0	16.00	17.4	1.4	17.18	16.9	0.3	30.18	27.8	2.3	14.00	15.0	1.0	84.6	83.3	1.3
42	4.6			9.89			26.28			15.75			47.17			103.7		
42	5.4	5.0	0.4	11.30	10.6	0.7	18.09	22.2	4.1	16.00	15.9	0.1	47.44	47.3	0.1	98.2	101.0	2.7
84	1.1			3.79			32.28			2.07			66.59			105.8		
84	2.0	1.6	0.4	3.75	3.8	0.0	21.34	26.8	5.5	4.21	3.1	1.1	64.21	65.4	1.2	95.5	100.7	5.2
																	100.1	9.0

[1]Results (% of applied radioactivity) from Annex G, p. 43 of the study report.
[2]Results (% of applied radioactivity) from Annex G, p. 45 of the study report.
[3]Results (% of applied radioactivity) calculated by primary reviewer using sample radioactivity (in Bq) from Annex G, pp. 48-51 and initial radioactivity applied (in Bq) from Annex G, p. 42 of the study report. Example, KR 84D A = (115777 Bq/358696 Bq)*100 = 32.28% of appli
[4]Results (% of applied radioactivity) calculated by primary reviewer using sample radioactivity (in Bq) from Annex G, p. 44 and initial radioactivity applied (in Bq) from Annex G, p. 42 of the study report.
[5]Results (% of applied radioactivity) calculated by primary reviewer using sample radioactivity (in Bq) from Annex G, p. 52 and initial radioactivity applied (in Bq) from Annex G, p. 42 of the study report.
[6]Not analyzed.
Means and standard deviations calculated using Corel Quattro Pro 8 program functions @avg(A1..A2) and @std(A1..A2).

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

Kromme Rijn Water-Sediment.
Determination of total radioactivity associated with sediment.

	Sediment				
	Ext	Nonext	Total		
Day	%AR	% AR	% AR	Mean	s.d.
0	0.27	0.37	0.6		
0	0.26	0.35	0.6	0.6	0.0
1	0.33	0.62	1.0		
1	0.37	0.49	0.9	0.9	0.0
3	3.01	1.93	4.9		
3	7.92	5.07	13.0	9.0	4.0
7	8.79	2.80	11.6		
7	9.90	4.42	14.3	13.0	1.4
14	17.77	7.32	25.1		
14	17.46	7.85	25.3	25.2	0.1
28	18.86	16.54	35.4		
28	16.00	17.18	33.2	34.3	1.1
42	9.89	26.28	36.2		
42	11.30	18.09	29.4	32.8	3.4
84	3.79	32.28	36.1		
84	3.75	21.34	25.1	30.6	5.5

[14C]Residue water phase:sediment ratios.

	Water	Sed	Ratio	Ratio	Mean	s.d.	Mean	s.d.
Day	% AR	% AR	W:S	S:W	W:S ratio		S:W ratio	
0	101.8	0.6	160	0				
0	89.1	0.6	146	0	153	7	0	0
1	102.3	1.0	107	0				
1	101.7	0.9	118	0	113	5	0	0
3	110.8	4.9	22	0				
3	94.9	13.0	7	0	15	8	0	0
7	92.3	11.6	8	0				
7	89.2	14.3	6	0	7	1	0	0
14	65.8	25.1	3	0				
14	67.9	25.3	3	0	3	0	0	0
28	5.2	35.4	0	7				
28	7.2	33.2	0	5	0	0	6	1
42	4.6	36.2	0	8				
42	5.4	29.4	0	5	0	0	7	1
84	1.1	36.1	0	33				
84	2.0	25.1	0	13	0	0	23	10

Results (% of applied radioactivity) from Annex G, pp. 43, 45 of the study report and calculated results (% of applied) using sa radioactivity results (in Bq) from Annex G, pp. 42, 48-51.
Means and standard deviations calculated using Corel Quattro Pro 8 program functions @avg(A1..A2) and @std(A1..A2).

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

Determination of total $^{14}CO_2$ for entire system.
TNO Water-Sediment.

	$^{14}CO_2$				
	In H_2O	Volatile	Total		
Day	%AR	% AR	% AR	Mean	s.d.
0	NA[1]	NA	0.0		
0	NA	NA	0.0	0.0	0.0
1	1.24	0.08	1.3		
1	1.25	0.25	1.5	1.4	0.1
3	1.33	0.31	1.6		
3	0.96	0.43	1.4	1.5	0.1
7	1.20	0.75	1.9		
7	0.90	0.69	1.6	1.8	0.2
14	2.01	1.07	3.1		
14	1.71	1.45	3.2	3.1	0.0
28	28.38	14.58	43.0		
28	32.92	17.47	50.4	46.7	3.7
42	14.74	37.58	52.3		
42	18.38	35.50	53.9	53.1	0.8
84	3.30	53.56	56.9		
84	5.75	50.54	56.3	56.6	0.3

[1]Not analyzed.
Results imported from **TNO Mat bal** worksheet.

Determination of total $^{14}CO_2$ for entire system.
Kromme Rijn Water-Sediment.

	$^{14}CO_2$				
	In H_2O	Volatile	Total		
Day	%AR	% AR	% AR	Mean	s.d.
0	NA	NA	0.0		
0	NA	NA	0.0	0.0	0.0
1	1.79	0.21	2.0		
1	1.54	0.16	1.7	1.8	0.1
3	1.61	0.24	1.8		
3	1.39	0.30	1.7	1.8	0.1
7	1.22	0.70	1.9		
7	1.07	0.83	1.9	1.9	0.0
14	1.63	1.95	3.6		
14	2.12	1.68	3.8	3.7	0.1
28	25.51	15.93	41.4		
28	30.18	14.00	44.2	42.8	1.4
42	15.75	47.17	62.9		
42	16.00	47.44	63.4	63.2	0.3
84	2.07	66.59	68.7		
84	4.21	64.21	68.4	68.5	0.1

[1]Not analyzed.
Results imported from **KR Mat bal** worksheet.

Means and standard deviations calculated using Corel Quattro Pro 8 program functions @avg(A1..A2) and @std(A1..A2).

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

Determination of means/standard deviations for [^{14}C]MCPA.

TNO Water-Sediment[1].

	MCPA								
	Water			Sediment			Total System		
Day	% AR	Mean	s.d.	% AR	Mean	s.d.	% AR	Mean	s.d.
0	94.2			1.5			95.7		
0	88.0	91.1	3.1	0.5	1.0	0.5	88.5	92.1	3.6
1	87.0			0.6			87.6		
1	89.1	88.1	1.0	0.8	0.7	0.1	89.9	88.8	1.1
3	110.7			2.8			113.5		
3	110.9	110.8	0.1	2.6	2.7	0.1	113.5	113.5	0.0
7	80.3			9.1			89.4		
7	74.9	77.6	2.7	7.6	8.4	0.7	82.5	86.0	3.5
14	66.7			16.0			82.7		
14	55.8	61.3	5.5	19.3	17.7	1.7	75.1	78.9	3.8
28	10.0			9.3			19.3		
28	2.8	6.4	3.6	7.7	8.5	0.8	10.5	14.9	4.4
42	3.9			7.3			11.2		
42	5.0	4.5	0.5	6.8	7.1	0.2	11.8	11.5	0.3
84	1.5			2.1			3.6		
84	1.3	1.4	0.1	2.6	2.4	0.2	3.9	3.8	0.2

Kromme Rijn Water-Sediment[2].

	MCPA								
	Water			Sediment			Total System		
Day	% AR	Mean	s.d.	% AR	Mean	s.d.	% AR	Mean	s.d.
0	101.8			0.3			102.1		
0	89.1	95.5	6.4	0.3	0.3	0.0	89.4	95.8	6.3
1	102.3			0.3			102.6		
1	101.7	102.0	0.3	0.4	0.4	0.1	102.1	102.4	0.3
3	110.8			3.0			113.8		
3	94.9	102.9	8.0	7.9	5.5	2.5	102.8	108.3	5.5
7	92.3			8.8			101.1		
7	89.2	90.8	1.5	9.9	9.4	0.5	99.1	100.1	1.0
14	65.8			17.8			83.6		
14	67.9	66.9	1.1	17.5	17.7	0.2	85.4	84.5	0.9
28	5.2			9.6			14.8		
28	7.2	6.2	1.0	7.1	8.4	1.3	14.3	14.6	0.3
42	4.6			2.7			7.3		
42	5.4	5.0	0.4	3.0	2.9	0.1	8.4	7.9	0.6
84	1.1			3.8			4.9		
84	2.0	1.6	0.4	3.8	3.8	0.0	5.8	5.4	0.5

[1]Results (% of applied radioactivity) from Annex H, p. 55 of the study report.
[2]Results (% of applied radioactivity) from Annex H, p. 58 of the study report.
Means and standard deviations calculated using Corel Quattro Pro 8 program functions @avg(A1..A2) and @std(A1..A2).

Aerobic Aquatic Metabolism of [Phenyl-U-^{14}C]MCPA.
MRID 45889303

Determination of means/standard deviations for [^{14}C]MCPA.

TNO Water-Sediment[1].

	Metab 1			Metab 2		
	Sediment			Sediment		
Day	% AR	Mean	s.d.	% AR	Mean	s.d.
0						
0		ERR	ERR		ERR	ERR
1						
1		ERR	ERR		ERR	ERR
3						
3		ERR	ERR		ERR	ERR
7						
7		ERR	ERR		ERR	ERR
14						
14		ERR	ERR		ERR	ERR
28	4.3			5.9		
28	1.2	2.8	1.5	4.0	5.0	1.0
42						
42		ERR	ERR		ERR	ERR
84						
84		ERR	ERR		ERR	ERR

Kromme Rijn Water-Sediment[2].

	Metab 1			Metab 2		
	Sediment			Sediment		
Day	% AR	Mean	s.d.	% AR	Mean	s.d.
0						
0		ERR	ERR		ERR	ERR
1						
1		ERR	ERR		ERR	ERR
3						
3		ERR	ERR		ERR	ERR
7						
7		ERR	ERR		ERR	ERR
14						
14		ERR	ERR		ERR	ERR
28				9.3		
28		ERR	ERR	8.9	9.1	0.2
42	2.6			4.6		
42	3.0	2.8	0.2	5.2	4.9	0.3
84						
84		ERR	ERR		ERR	ERR

[1]Results (% of applied radioactivity) from Annex H, p. 55 of the study report.
[2]Results (% of applied radioactivity) from Annex H, p. 58 of the study report.
Means and standard deviations calculated using Corel Quattro Pro 8 program functions @avg(A1..A2) and @std(A1..A2)

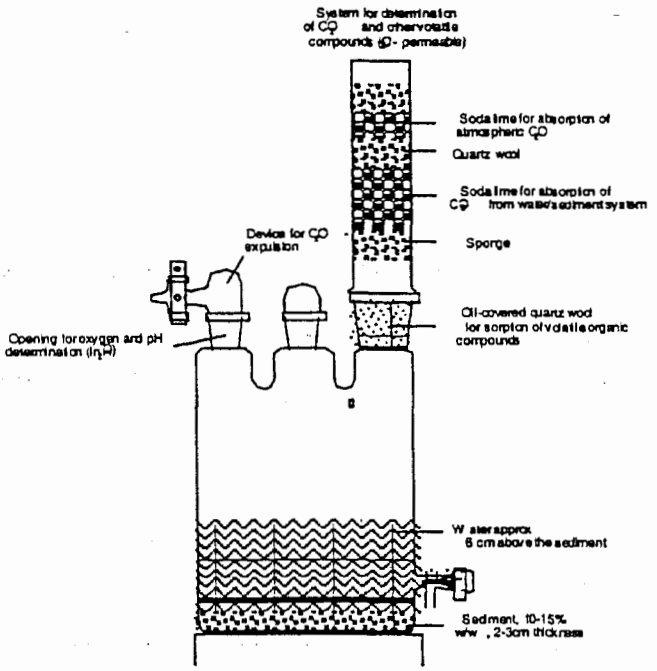


Figure 1 *The incubation vessel*

Ditch water was placed in each biometer flask, together with a sufficient amount of its matching wet sediment to form 3-cm layer on the bottom of the flasks; the total volume was 600 ml.
For the TNO test systems, 300 g of wet sediment (corresponding to 140 g dry solids) and 400 ml of TNO water were used. For the Kromme Rijn test systems, 300 g of wet sediment (corresponding to 128 g of dry solids) and 400 ml of Kromme Rijn water were used.
The flasks were pre-incubated on a rotary shaker (about 50 rpm) for 19 days at room temperature (±20 °C) in the dark. This experimental design made it possible to achieve the required aerobic environment in the upper section of the water column while maintaining undisturbed anaerobic sediment.

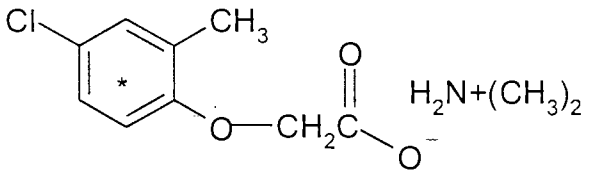
2.2.3 Preparation of test flasks and addition of stock solutions

Number of flasks
Fourteen biometer flasks of each sediment, prepared as described in section 2.2.2, were used for the experiment. Additionally, two ordinary bottles of each sediment were used for day 0. For the validation, two flasks (day 4 and 7) and one bottle (day 0) of each sediment were used.

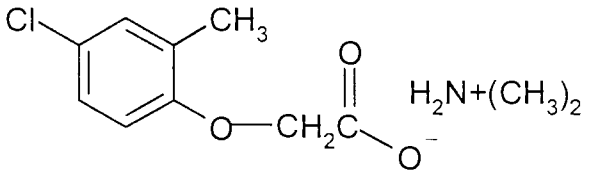
Attachment 2

Structures of Parent and Transformation Products

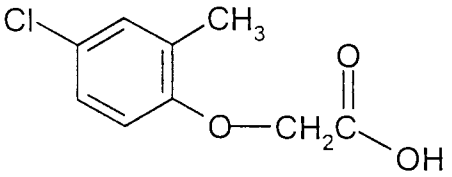
Structure of MCPA (with radiolabel)



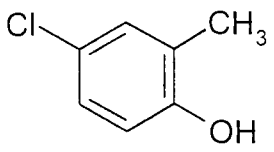
Structure of MCPA (without radiolabel)



Structure of 4-Chloro-2-methylphenoxyacetic acid



Structure of 4-chloro-o-cresol



Attachment 3

Illustration of Test System

13544

R148644

Chemical: MCPA (and salts and esters)

PC Code:
030501

HED File Code: 61400 SRRD DERs
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